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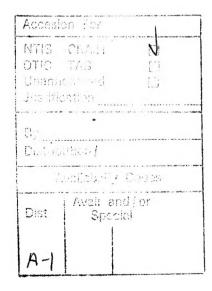| 17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
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13. ABSTRACT

The relaxation of molecular impurities in glasses has been gaining attention in recent years, partly due to the availability of novel spectroscopic techniques in the infrared region, including the development of powerful tunable infrared lasers needed to excite the vibrational transitions that are about 4 orders of magnitude weaker than electronic transitions. In general, glassy hosts offer the possibility to study the influence of a distribution the local environments on the static and dynamic properties of impurity atoms and molecules.

Both persistent hole burning and picosecond IR pump-probe measurements show that the low temperature vibrational relaxation time of SH in As_2S_3 is also quite fast ($\sim10^{-10}$ sec) even though temperature dependent measurements indicate that it corresponds to a seven phonon process. Equally interesting is that the relaxation time varies by a factor 6 across the inhomogeneously broadened band indicating a site-dependent interaction of the molecule with the host. A temperature dependence study indicated that the stretch mode relaxes through a multi-vibrational decay into modes of the glass host. We have also investigated the site-dependent vibrational relaxation dynamics of the OH molecular impurity in amorphous SiO_2. At low temperatures, a short relaxation time of the order of 10^{-10} sec is found that varies strongly across the inhomogeneously broadened absorption line, decreasing with increasing perturbation of the molecule by the host, similar to the results observed from As_2S_3:SH. A simple relation between the vibrational lifetime and the site-dependent frequency shift is found for both defect:glass systems by assuming that the molecule-host coupling determines both the shift of the vibrational frequency and the relaxation dynamics.

14. SUBJECT TERMS

molecular impurities, chalcogenide glass, tunable infrared lasers, persistent hole burning, picosecond pump-probe, vibrational lifetime, nonradiative decay.

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II. Summary of Completed Project

The relaxation of molecular impurities in glasses has been gaining attention in recent years, partly due to the availability of novel spectroscopic techniques in the infrared region, including the development of powerful tunable infrared lasers needed to excite the vibrational transitions that are about 4 orders of magnitude weaker than electronic transitions. In general, glassy hosts offer the possibility to study the influence of a distribution the local environments on the static and dynamic properties of impurity atoms and molecules.

Both persistent hole burning and picosecond IR pump-probe measurements show that the low temperature vibrational relaxation time of SH in As_2S_3 is also quite fast ($\sim 10^{-10}$ sec) even though temperature dependent measurements indicate that it corresponds to a seven phonon process. Equally interesting is that the relaxation time varies by a factor 6 across the inhomogeneously broadened band indicating a site-dependent interaction of the molecule with the host. A temperature dependence study indicates that the stretch mode relaxes through a multi-vibrational decay into modes of the glassy host. We have also investigated the site-dependent vibrational relaxation dynamics of the OH molecular impurity in amorphous SiO_2. At low temperatures, a short relaxation time on the order of 10^{-10} sec is found that varies strongly across the inhomogeneously broadened absorption line, decreasing with increasing perturbation of the molecule by the host, similar to the results observed for As_2S_3:SH. A simple relation between the vibrational lifetime and the site-dependent frequency shift is found for both defect:glass systems by assuming that the molecule-host coupling determines both the shift of the vibrational frequency and the relaxation dynamics.

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III. Technical Information

A. Description

For small matrix isolated molecules, persistent hole burning[1] and photon echo[2] experiments probe the dephasing of vibronic excitations, while transient saturation experiments[3,4] can be used to extract the energy decay time. The transfer of vibrational energy from small molecules to the condensed matter host is a topic of increasing experimental activity since decay times differing by many orders of magnitude have been found. The diatomic molecules CO in van der Waals crystals and CN- in ionic crystals, for example, show sufficiently long (~msec) decay times to be studied by vibrational fluorescence [5,6], but other molecules are not accessible by this technique because the nonradiative decay times are too short. Of particular current interest are the relaxation properties of molecules in glassy hosts, where both the effect of site dependent disorder and the dynamics of amorphous systems can be studied. Short times (subnanosec) have been reported for the OH stretch mode in fused silica, where a decay process into 4 lower frequency vibrational modes of the glass has been proposed [7]. Here we report on IR pump-probe measurements for a related small molecule-covalent glass system: the SH stretch mode in As_2S_3 glass.

The measurement of the vibrational relaxation time of the SH stretch mode in hydrogenated As2S3 glass provides an important test of the earlier OH-fused silica multi-quanta hypothesis. Due to the lack of high frequency excitations in the As_2S_3 glass [8], at least 7 vibrational quanta are required to match the SH stretch mode energy. Thus, a longer lifetime is expected for a relaxation due to a 7th order process compared to the 4th order process for OH doped silica glass if the lifetime depends mainly on the order of the relaxation mechanism.

A further reason for this study relates to the earlier persistent infrared hole burning measurements on the SH stretch mode in hydrogenated As_2S_3 glass samples at low temperatures [9]. This study revealed a strong frequency dependence of the persistent hole width within the inhomogeneously broadened SH absorption band. The proposed explanation for the variable relaxation time is a frequency dependent coupling of the stretch mode vibration to the matrix.

Although persistent hole burning experiments provide information about the total dephasing time only, the decay time can be estimated with the additional assumption that there

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are no other dynamical processes such as spectral diffusion [10] and that the energy relaxation time determines the homogeneous line width at low temperature. The obvious advantage of performing picosecond pump-probe measurements is the direct measurement of the pure energy relaxation time T_1, which allows us to test the proposition that pure dephasing does not contribute to the hole width at low temperature.

A picosecond infrared pump-probe saturation technique is used to determine the energy relaxation rate T_1. A strong IR pump pulse excites a fraction of the SH oscillators to the first excited $n = 1$ vibrational state. Due to anharmonicity of the mode, the $n \geq 2$ transition is not resonant with the pump pulse, thus the population in the first vibrational level leads to a bleaching of the absorption. After the excitation, the population returns to its equilibrium value due to the relaxation of the excited vibrational state with a time constant T_1. The relaxation is probed by a weak probe pulse as a function of a delay Δt between the pump and probe pulse.

Tunable IR picosecond laser pulses, resonant with the SH $(0 \rightarrow 1)$ transition, are generated by difference mixing the radiation of a modified Continuum PD10 dye laser and a Continuum PY61 active-passive mode locked YAG laser in a $LiNbO_3$ crystal. Energies of about 10 mJ per pulse are obtained at 2500 cm^{-1}. Care was taken to adjust the linewidth (FWHM) of the IR pulse, averaged over many laser pulses, to a value of about 4 cm^{-1}. The length of the infrared pulses is 15 psec and the repetition rate of the laser system is 10 Hz. A small fraction of the pulse is coupled into a monochromator equipped with an InSb detector to monitor the frequency. The main IR pulse is focused on the sample by means of an off-axis gold coated parabolic mirror. The saturation ($< 5\%$) of the SH absorption line is measured by a weak probe beam, split off from the main pump pulse, delayed with respect to the pump pulse on an optical delay line and detected by a thermoelectrically cooled PbSe detector, mounted on an integrating sphere. The sample is mounted on the cold finger of a temperature variable cryostat. To ensure a good thermal link, the 2 mm thick sample, cut and polished from a hydrogenated As2S3 ingot, is attached with indium to the copper block of the sample holder. The sample temperature is monitored by a calibrated carbon resistor.

The SH doped samples are prepared by melting pure As_2S_3 glass in a sealed quartz tube filled with hydrogen gas at one atmosphere. Upon first heating the tube to 500 C for 30 minutes and then air quenching, a strong stretch mode band is produced. The solid line in Fig. 2 shows the absorption spectrum of the hydrogenated As_2S_3 sample in the region of the SH

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absorption band at 1.5 K, with an absorption maximum at 2485 cm^{-1}. The width of the inhomogeneously broadened line is about 100 cm^{-1}, reflecting the influence of the disordered host on the stretch mode frequency. Low temperature relaxation times were measured at a sample temperature of 8 K in the frequency range between 2425 cm^{-1} and 2505 cm^{-1}. We find a frequency dependent lifetime that varies from 60 psec at 2425 cm^{-1} to 350 psec at 2502 cm^{-1}. Due to inadequate absorption, no relaxation times could be measured at lower or higher frequencies. Compared to the vibrational frequency of the free SH molecule at 2599 cm^{-1} [11], the frequencies of the SH molecules in the host are red shifted, which is the case when the coupling of the excited molecule to the host is stronger than that of the molecule in the ground state [12]. Thus, an SH molecule with a stretch mode at the high frequency side of the band is less strongly coupled than a molecule in the low frequency wing. We find that the decrease in the vibrational lifetime is directly related to an increased coupling to the glassy host. Also data extracted from the earlier hole burning experiments of Ref. [9], measured at a sample temperature of 1.5 K are in good agreement with these results. The plotted lifetimes are obtained under the assumption that the hole width at low temperature is determined by the energy relaxation time T_1.

The temperature dependence of the lifetime has been determined at three frequencies, 2466 cm^{-1}, 2494 cm^{-1} and 2503 cm^{-1}. For all the tested frequencies, the relaxation times remain constant up to a temperature of 90 K within the error of the experiment. At higher temperature the decay rate increases gradually, becoming a factor 4 larger at room temperature. As expected, this behaviour is quite different from the temperature dependence of the persistent spectral hole width, which broadens quadratically due to dephasing. In the temperature range between 1.5 K and 10 K this dephasing leads to a broadening of the hole width by a factor of 10 [9].

We have analyzed the temperature dependent lifetime data with a model where it is assumed that the SH vibration with frequency n relaxes into N host vibrational quanta of equal energy n/N. Thermal population of the vibrational modes of the glassy host at elevated temperatures leads to a stimulation of the relaxation process resulting in a temperature dependent relaxation rate T_1^{-1} [13]. Good agreement is found for N = 7 demonstrating that the SH stretch mode relaxes into 7 quanta, each with a frequency of about 355 cm^{-1}. A comparison with the vibrational spectrum for As_2S_3 glass indicates that this frequency

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coincides with the highest characteristic vibrational frequency of the excitation spectrum of the glass [8], consistent with the multi-vibration relaxation proposal.

Comparing the presented results with those found for the relaxation time of the OH stretch mode in fused silica[7], we find that the relaxation times of both are on the order of 100 psec at low temperatures, although the order of the respective decay processes is very different. Thus the fourth order decay process of OH mode in silica gives the same low temperature decay rate as the seventh order process of the SH mode in As_2S_3. In order to account for this similarity, the coupling constant must increase drastically from the OH-silica to the SH-chalcogenide system, even though both molecules are bonded covalently to their respective networks.

Since our direct pump-probe measurements have confirmed the indirect persistent hole burning lifetime measurements, there is a set of observations from that earlier work which now takes on new importance. The lifetime of the SD stretch mode was also estimated from measured persistent hole widths [9]. This stretch mode frequency is outside the range of our pump-probe system, but since the SH data agrees with the pump-probe results, there is reason to reexamine the SD data. In the high frequency wing the ratio of the narrowest persistent holes measured for SD/SH ~ 3/4. However, since multi-vibration decay would be a seventh order process for SH and a fifth order process for SD, the SD stretch mode should relax much faster than the SH mode and the SD/SH hole width ratio should be much larger than 1 in the multi-vibration decay picture. One way to make these data consistent with the decay model above would be to decrease the coupling of the SD molecule to the glass, indicating, as in the case of the comparison of the OH-silica and SH-As2S3 lifetimes, a dominant role of the coupling constant. A prediction of the multi-vibration decay model, which needs to be tested, is that the temperature dependence of the energy relaxation time for the SD stretch mode should follow the dash-dotted curve in Fig. 3, the dependence generated by a fifth order process.

In conclusion, we have measured the frequency and temperature dependence of the nonradiative relaxation time of the first excited state of the SH vibrational mode in hydrogenated As_2S_3 glass. Within the inhomogeneously broadened band, a strong decrease in the low temperature lifetime is found for increased coupling to the host. Our findings agree with the frequency dependence of the low temperature line width found in persistent IR spectral

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hole burning experiments. The similarity of the results from both types of experiments show that the persistent hole width at low temperature is dominated by the energy relaxation time T1. The temperature dependence of the energy relaxation time can be explained within the framework of multi-vibrational relaxation, where the stretch mode relaxes into 7 quanta of the high frequency peak in the density of vibrational states of the glass network. We find a low temperature SH lifetime in the chalcogenide glass comparable to that of OH in fused silica, even though the orders of the processes are very different. This indicates that the magnitude of the coupling coefficient, not the order of the process, is the key ingredient in the decay dynamics for stretch modes of small molecules in these amorphous systems.

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